ANALYTICAL

UNDERGRADUATE EXPERIMENT

Alcohol Identification via ^{13}C NMR Spectroscopy

INTRODUCTION

The use of nuclear magnetic resonance (NMR) spectrometers to characterize chemical species is well established in chemistry. Still, the incorporation of this technique in undergraduate laboratories for structural elucidation and quantification purposes has yet to be adopted by many institutions. The slow uptake of a hands-on approach to NMR in these settings is largely due to the extensive costs, space requirements, and training needed to use traditional high-field NMR spectrometers. With the evolution of benchtop NMR spectrometers, a void has been filled for this invaluable technique in underserved sectors. As such, there has been a corresponding shift to a more hands-on approach to NMR in teaching environments. However, low-field NMR spectrometers are different than their high-field counterparts; this should be evident given their differences in field strength, which leads to differences in sensitivity and dispersion (including resolution).[1]

Undergraduate students are taught ^{1}H NMR spectroscopy in first- or second-year organic chemistry courses where concepts such as integration, multiplicity, chemical equivalence, and chemical shift are discussed. This wealth of information can oftentimes be overwhelming and lead to confusion in a classroom setting. A way to circumvent this dilemma is to teach ^{13}C NMR spectroscopy first in a hands-on laboratory setting. Introducing carbon (proton-decoupled) NMR is advantageous as it simplifies this characterization technique to a more manageable level. Students do not need to worry about multiplicity and integration and can focus on chemical shift and equivalence until they have a proper grasp of these basic concepts. In addition, heteronuclei have a larger chemical shift range when compared to ^{1}H NMR and as a result, less potential for overlapping of signals which could further complicate this learning process.

In this experiment, adapted from an article published in The *Journal of Chemical Education* by Chamberlain, a suite of ^{13}C NMR experiments was chosen to enable students to identify various alcohols (**Table 1**) based on chemical shift and chemical equivalence.[2]

Table 1. Number of resonances in ^{13}C NMR spectra of various alcohols[2]

		Number of Peaks			
Alcohol	^{13}C	CH	CH_2	CH_3	CR_4
4-Methyl-2-pentanol	5	2	1	2	0
1-Pentanol	5	0	4	1	0
4-Methylcyclohexanol	5	2	2	1	0
1-Hexanol	6	0	5	1	0
2-Methyl-1-pentanol	6	1	3	2	0
2,2,4-Trimethyl-1-pentanol	6	1	2	2	1
2-Methylcyclohexanol	7	2	4	1	0
3,5,5-Trimethyl-1-hexanol	7	1	3	2	1
2-Phenyl-2-butanol	10	5	1	2	2
Geraniol	10	2	3	3	2
Eugenol	10	4	2	1	3
Linalool	10	2	3	3	2

Due to the unique structure of each compound presented in **Table 1**, students will be able to distinguish between these based on the total number of carbon signals, -CH signals, -CH_2 signals, -CH_3 signals, and CR_4 signals. This information is easily gathered using regular $^{13}C\{^1H\}$ NMR experiments, the trio of distortionless enhancement by polarization transfer (DEPT) experiments, and the attached proton test (APT), where:

$^{13}C\{^1H\}$ shows all signals in the positive phase
DEPT-135 shows -CH and -CH_3 peaks in the positive phase and -CH_2 peaks in the negative phase
DEPT-90 shows only -CH resonances in the positive phase
DEPT-45 shows all -CH/-CH_2/-CH_3 resonances in the positive phase
APT shows -CH and -CH_3 resonances in the positive phase and -CH_2 and CR_4 in the negative phase

Oftentimes, only APT or $^{13}C\{^1H\}$ NMR is acquired, along with DEPT-135 and DEPT-90 to assign the various moieties as shown in **Table 1**. For thoroughness, all experiments were run for this study.

PROCEDURE

The unknown alcohol (0.6 mL) was added into a standard 5 mm diameter NMR tube. A series of ^{13}C NMR spectra ($^{13}C\{^1H\}$, DEPT-135, DEPT-90, DEPT-45, and APT) was collected for each of the unknown alcohol samples using the 60PRO instrument (spectral width: 220 ppm, spectral center: 100 ppm, number of points: 4096, number of scans: 64, scan delay: 0s). The queuing functionality was used for this experiment, and all spectra were gathered without the use of deuterated solvents.

RESULTS AND DISCUSSION

Figure 1 depicts the structure of eugenol and linalool, while **Figure 2** and **Figure 3** display six different spectra of each of the respective compounds. The ^1H spectra (**Figure 2A** and **3A**) of both compounds are complex and show overlapping signals, making differentiation difficult between both compounds. The $^{13}C\{^1H\}$ NMR spectrum (**Figure 2B** and **3B**) of both eugenol and linalool show 10 resonances, but as both compounds each have 10 unique carbon centres, this information is not enough to discern between the two.

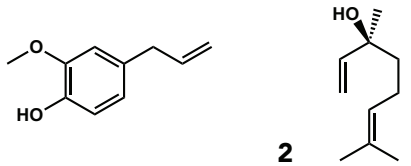

Figure 1. Molecular structures of eugenol (1) and linalool (2).

Fortunately, compounds **1** and **2** generate a unique set of DEPT and APT spectra. As seen in **Figure 2**, eugenol shows 7 signals in DEPT-45 **(F)**, four of which are -CH signals as shown in DEPT-90 **(E)**, two of which are -CH_2 peaks, and one of which is a -CH_3 group (minus the -CH groups from DEPT-90) as shown in DEPT-135 **(D)**. The APT NMR spectrum **(C)** shows three quaternary carbon centers.

As seen in **Figure 3**, linalool shows 8 signals in DEPT-45 **(F)**, two of which are -CH signals as shown in DEPT-90 **(E)**, three of which are -CH_2 peaks, and three are -CH_3 group (minus the -CH groups from DEPT-90) as shown in DEPT-135 **(D)**. The APT NMR spectrum **(C)** shows two quaternary carbon centers.

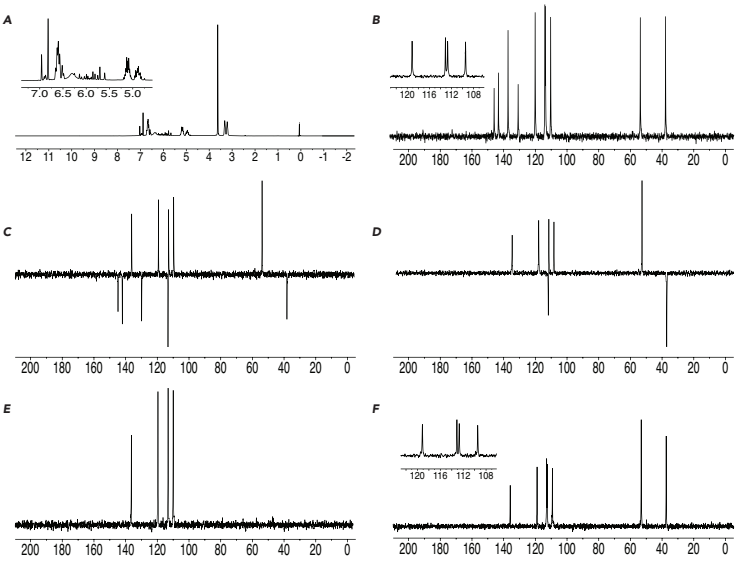

Figure 2. Various NMR spectra of neat eugenol. A) ^1H (60 MHz) NMR spectrum with added TMS as an internal chemical shift reference. B) $^{13}C\{^1H\}$ (15.1 MHz) NMR spectrum. C) APT NMR spectrum. D) DEPT-135 NMR spectrum. E) DEPT-90 NMR spectrum. F) DEPT-45 NMR spectrum.

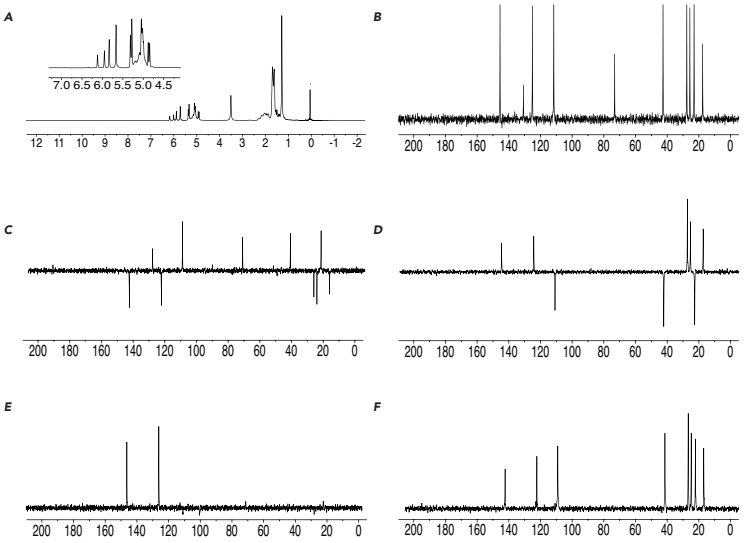

Figure 3. Various NMR spectra of neat linalool. A) ^1H (60 MHz) NMR spectrum with added TMS as an internal chemical shift reference. B) $^{13}C\{^1H\}$ (15.1 MHz) NMR spectrum. C) APT NMR spectrum. D) DEPT-135 NMR spectrum. E) DEPT-90 NMR spectrum. F) DEPT-45 NMR spectrum.

By considering the ^{13}C NMR spectral data in combination with the structure of each compound, students can match up and determine which unknown set of spectra correlates to which compound. **Table 1** can be constructed by analyzing the structure of each unknown alcohol prior to the acquisition of NMR data.

CONCLUSION

In this experiment, the differentiation of alcohols was determined using a suite of ^{13}C experiments. The resulting spectra obtained from the range of DEPT experiments clearly distinguished the different compounds presented in **Table 1**, as each species had a unique number of -CH, -CH_2, -CH_3, and CR_4 moieties. Furthermore, heteronuclear NMR spectroscopy was introduced to mitigate the difficulties of teaching ^1H NMR spectroscopy in a classroom setting.

References

[1] Araneda, J.F.; Barbosa, T.M.; Hui, P.; Leclerc, M.C.; Ma, J.; Maier, A.F.G.; Riegel, S.D. *J. Chem. Ed.* **2021**, *98*, 1227-1232.
[2] Chamberlain, P.H. *J. Chem. Ed.* **2013**, *90*, 1365-1367.